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CHRONICLE

SESSION OF THE DEPARTMENT OF CHEMICAL SCIENCES
OF THE ACADEMY OF SCIENCES USSR, HELD
15-16 OCTOBER 1959

By L. G. Makarova

- USSR -

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Following is the translation of an article written by L.G. Makarova, which was published in Izvestiya Akademii Nauk SSSR - Otdeleniye Khimicheskikh Nauk (Bulletin of Academy of Sciences USSR, Division of Chemical Science) No 2, Moscow, Feb 1960, pp 378-381.

On 15 thru 16 October 1959, in Moscow, the Department of Chemical Sciences and the scientific board of the Institute of Elementary Organic Compounds, held a joint session for the purpose of celebrating the 60th birthday of Aleksander Nikolayevich Nesmeyanov, president of the Academy of Sciences USSR, and director of the Institute of Elementary Organic Compounds.

The Session, which took place in the Institute of Organic Chemistry, was opened by academician M.M. Shemyakin, who gave a hearty welcome to academician A.N. Nesmeyanov, and described his activities in the capacity of a director of the largest chemical school in the Soviet Union. The chairman proceeded to stress the wide range of A.N. Nesmeyanov's scientific activity, beginning with his brilliant studies of the theory of organic chemistry and his fine syntheses based on β -chlorotinylketones up to his work which led to the discovery of multi-tonnage, high-molecular compounds that at the present time are already being used in practice.

Thereafter academician A.N. Nesmeyanov took the floor. Nesmeyanov's report was devoted to the section of his work which concerned synthesis and study of the properties of diaryl-halogenium and triaryl-oxonium compounds. This field of investigations in which Aleksander Nikolayevich has worked extensively during the past time, overlaps with his first works on the decomposition of bi-

diazonium salts with mercuric iodide, the thermal decomposition of which has led to the discovery of diaryl iodonium salts. On the other hand, the thermal decomposition of the double salt of aryl diazonium bromide with mercuric bromide, as has been lately shown, produces diaryl bromonium salts. The works in the field of diaryl halogenium salts and triaryl oxonium salts were preceded by investigations to study the mechanism of the decomposition of aryl diazonium and diaryl iodonium salts. As a result of these investigations, it was found that aryl diazonium and diaryl iodonium salts can decompose not only homolytically but also heterolytically, depending on the nature of the anion. The decomposition of borofluorides of aryl diazonium and diaryl iodonium is heterolytic, and forms an aryl cation in the process. Arylation of bromobenzene, chlorobenzene, diphenyl oxide with an aryl cation formed in the decomposition of the boron fluorides of aryl diazonium, produced for the first time the hitherto unknown diaryl bromonium, diaryl chlorinium and triaryl oxonium salts. The properties and reactions of these most interesting compounds have been extensively investigated. It has been shown that the stability of these compounds depends on the nature of the anion. It has been found that the newly discovered diaryl halogenium salts are subject to decomposition, and that they are able to arylate both according to the heterolytical mechanism (arylation of the anions of amine salts) and to the homolytical mechanism (arylation of metals). Characteristic of triaryl oxonium salts is their unexpectedly high stability; these decompose only at high temperatures, and show no inclination toward arylation reactions. The nitration reactions of triphenyl oxonium and diaryl halogenium salts demonstrate that the diphenyl oxonium group is an orientator of the first order, while the aryl halogenium group orients the electrophilic attack both in the meta- and the para position.

P.Kh. Freydlina, corresponding member of the Academy of Sciences USSR, reported on the methods of the synthesis of electroorganic compounds developed in the school of A.N. Nesmeyanov. She spoke of the creation of different methods of synthesis, among others, of the "chemical ways of communication" which A.N. Nesmeyanov considers to be one of the most important problems in the chemistry of elementary organic compounds. As a result of many years of investigation, the school of A.N. Nesmeyanov developed interconversion paths of chemical compounds for a large

number of elements belonging to nearly every group of the periodic system. In the works of A.N. Nesmeyanov, the development of synthesis methods is closely associated with the investigations of the mechanism of reactions. In synthesis, A.N. Nesmeyanov made extensive use of different mechanisms of the breaking of chemical bonds in a molecule. Thus, the "onium" method of synthesis developed by A.N. Nesmeyanov permits utilization both of the homolytical type (synthesis of metalorganic compounds) and the heterolytical type (synthesis of diaryl halogenium, triaryl oxonium compounds and other) of "onium"-compound decomposition. The unlike mechanisms of the interchange reactions of elementary organic compounds with substances of the electrophilic, nucleophilic, and radical types, are extensively used in the synthesis of new elementary organic compounds. A.N. Nesmeyanov does not shut himself up in the narrow frames of particular problems relating to synthesis. Problems of synthesis solved by A.N. Nesmeyanov were, first of all, dictated by the requirements of socialist construction. On the other hand, in the selection of these problems, A.N. Nesmeyanov is guided by profound studies of the interdependence between the structure of an atom and its ability to form elementary organic compounds.

In her report, under the title "Diazosynthesis of metalorganic compounds", L.G. Makarova, Dr of Chem. Sc., spoke of the significant contribution to science in the form of the universal method of the synthesis of aromatic metalorganic compounds, developed by A.N. Nesmeyanov in 1929; further, of the method of double diazonium salts, known as the diazo-method, which consists in the decomposition of aryl-diazonium double salts with the halides of metals under the effect of a reducing agent. The diazo-method, which was first developed after the example of mercurio-organic compounds, permits obtaining these compounds with a diversity of substitutes within an aromatic nucleus; it was also extended to serve the synthesis of mercurio-organic compounds of the heterocyclic series and, recently, of the alicyclic and aliphatic series. Further, the diazo-method was developed for the synthesis of the aromatic compounds of other metals, such as antimony, arsenic, bismuth, thallium, tin, germanium, lead, as well as selenium. The extensive possibilities of obtaining various types of metalorganic compounds on the basis of the diazo-method, were disclosed. The feasibility of synthesizing, by means of the diazo-method, the various

groups of mercuro-organic compounds, which are the key-compounds among metalorganic ones, permits utilization of these compounds to obtain certain, hitherto, unknown forms of the aromatic compounds of zinc, tin, aluminum, thallium, lead and germanium. The school headed by A. N. Nesmeyanov has developed in detail diverse variations of the synthesis of metalorganic compounds on the basis of the diazo-method, and this enables us to select the most efficient form of the diazo-synthesis of an organic compound of a metal.

Works written on the diazo-method gave rise to a series of other works which deal with the investigation of the mechanism of its course. Both Nesmeyanov and the speaker indicated that diazonium and other onium compounds are susceptible to both homolytic and heterolytic decomposition involving the formation of aryl cations. Once having been accomplished, the heterolytic decomposition of aryl-diazonium salts found widespread application in the field of synthesis. It has been proved that a heterolytic decomposition of diazonium salts is converted into a homolytic one on account of the presence of metals. This fact suggests that the synthesis of metalorganic compounds on the basis of the diazo-method also proceeds in a homolytic fashion.

O.A. Reutov, corresponding member of the Academy of Sciences, spoke in his lecture under the title "Stereochimistry as a Reaction of Electrophilic and Homolytic Substitution in a Saturated and an Ethylene Carbon Atom," of the results of separate investigations conducted by two groups of Nesmeyanov's pupils, one composed of A.E. Borisov, Dr. Chem. Sc., and his collaborators in the "INECS", and the other of the lecturer and his collaborators in the "MGU". As a result of the study of a great number of interconversions of β -vinylchloride and isopropenyl cis- and trans-metalorganic compounds of mercury, antimony, tin, thallium and lead, it was demonstrated that stereochemical configuration was preserved in the course of these conversions. This allowed A.N. Nesmeyanov and A.E. Borisov to express the rule of the conservation of geometric configuration in electrophilic and homolytic substitution reactions in the unsaturated atoms of carbon. Later on, this rule was directly confirmed in the study of electrophilic and homolytic reactions of isotope exchange for vinylchloride compounds of mercury. The mechanism of electrophilic and homolytic substitution

reactions of a saturated carbon atom has been studied. The S_p -2 rule of conservation of stereochemical configuration in the course of bimolecular reactions of electrophilic substitution in a saturated carbon atom, has been derived as a result of the investigations of the stereochemistry and kinetics of reactions of the symmetrization of mercurio-organic salts, and the reactions of inverse symmetrization, as well as of reactions of isotope exchange between mercurio-organic salts and halides of mercury. Based on the study of homolytic reactions of isotope exchange between mercury-organic salts and metallic mercury, one has arrived at the conclusion pertaining to the preservation of configuration in homolytic reactions, involving saturated carbon atoms.

The last report of the 15th October meeting was made by E.G. Perevalova, Cand. Chem. Sc., who, in her own behalf, spoke to N.A. Vol'kenau, N.S. Kochetkova and V.A. Sazanova of the investigations in the field of complexing to form ferrocene compounds conducted under the direction of N.A. Nesmeyanov. The chemical properties of the unusual ferrocene system are thoroughly and widely studied by Nesmeyanov and his collaborators. The numerous reactions of hydrogen-atom exchange in ferrocene complexes, which have proved its aromatic nature, have been extensively investigated. It has been demonstrated that ferrocenes readily react in electrolytic and homolytic substitutions. Ferrocene, and the various substituted ferrocenes obtained, have been investigated with respect to their mercurization, metallization with lithium- and sodium alkyls, alkylation and acylation according to Friedel Krafts, sulfonation and arylation. A large number of various derivatives of ferrocene, such as alkyl-, carbonic- and boric-acids, hydroxyferrocene, selenic derivatives of ferrocene, ferrocenylamine, azo-ferrocene, ferrocene halides, diferrocetyl, have been synthesized by way of further conversion of substituted ferrocene obtained. The previously developed diazo-method (employing mercurioorganic compounds) permitted the derivation of these compounds with greatest number of substitutions in the aromatic nucleus. This method has also been applied in the synthesis of mercurioorganic compounds of the heterocyclic, and lately, of alycyclic and fatty order. The diazo-method was further developed for the synthesis of aromatic compounds of other metals - antimony, arsenic, bismuth, thallium, tin, germanium, lead, and also selenium. Numerous possibilities, made feasible through

the use of the diazo-method, in the derivation of various type of organometallic compounds, were indicated. An enormous scope of possibilities of synthesizing various types of mercurioorganic substances, offered by the diazo-method, permitted synthesis of certain key compounds, hitherto unknown, and their application in the derivation of the aromatic compounds of tin, aluminum, thallium, germanium, lead. At the Nesmeyanov's School there were widely developed different variations of the diazo-method applied to synthesis of metaloorganic substances, that resulted in the possibility of making selection and employing the most adoptible approach in the diazo-synthesis of organometallic substances of any metal in particular.

This work on the development of diazo-method generated a number of other investigations, devoted to the clarification of the mechanism involved. A. N. Nesmeyanov and the speaker have proved that the diazonium, as well as other "onium"- compounds, may decompose homolytically as well as heterolytically with the formation of aryl-cations. The initially accomplished heterolytic decomposition of the aryl diazonium salts was widely used for the purpose of synthesis. It was proved that the presence of metals transforms a heterolytic breakdown of diazonium salts into a homolytic breakdown which leads to an assumption, that synthesis of metaloorganic substances by the diazo-method also proceeds homolytically.

O. A. Reutov, Corresponding Member of the Academy of Science, USSR, in his paper entitled "Stereochemistry of the Reactions of Electrophilic and Homolytic Substitution of the Saturated and of the Ethylene Carbon Atom" presented the results of investigations conducted by the two groups of A. N. Nesmeyanov's pupils; Doctor of Chemical Sciences A. Ye. Borisov and coworkers of the INEOS and the speaker and his coworkers of the MGU. As a result of study of numerous conjugated conversions of β -chlorovinyl and isopropenyl cis- and trans- metaloorganic compounds of mercury, antimony, tin, thallium and lead, it has been demonstrated that these transformations take place with the preservation of stereo-chemical configuration. This lead A. N. Nesmeyanov and A. Ye. Borisov to formulate a rule pertaining to the preservation of the geometrical configuration of the carbon atom. This rule was then fully confirmed by the study of electrophilic and homolytic reactions of isotope exchange of the chlorovinyl compounds of mercury. Mechanism of the electrophilic substitution reactions involving saturated carbon atom was studied.

As the result of the investigation in stereochemistry and reaction kinetics of the symmetrization of the mercurorganic salts and of the reaction involving reversed symmetrization, as well as of the reactions covering isotope exchange of mercurorganic salts with haloidal mercury, the S₂-2 rule pertaining to the preservation of stereochemical configuration in the bi-molecular reactions of the electrophilic substitutions of saturated carbon atom has been derived. Based on the study of homolytic isotope exchange reaction of mercurorganic salts with metallic mercury, a conclusion has also been made regarding the preservation of configuration in the case of homolytic reactions involving saturated carbon atom.

The last presentation made at the meeting of October 15 was that the Candidate of Chemical Sciences - E. G. Perevalova, in the name of herself, N. A. Vol'kenau, N. S. Kochetkova and V. A. Sazonova devoted to study of ferrocene, conducted under direction of A. N. Nesmeyanov. Chemical properties of the unique ferrocene system were widely and thoroughly studied by Alexander Nikolayevich with his coworkers. Thoroughly studied were numerous substitution reactions of hydrogen atoms in ferrocene, which proved its aromatic nature, demonstrated that ferrocene undergoes reactions involving electrophilic and homolytic substitutions. Mercuriation and metallation of lithium and alkylation and acetylation with sodium alkyls in accordance with the Friedel-Kraft's, sulfonation and arylation of ferrocene as well as of the derived substituted ferrocenes were investigated. By way of further transformations of the obtained substituted ferrocenes, a great number of different ferrocene derivatives was synthesized such as: alkyl ferrocenes, carbonic and boric acids of ferrocene, oxy ferrocenes, selenium derivatives of ferrocene, ferroceneamines, azoferrocene, halogen derivatives of ferrocene, bisferrocenyl. Effect of substituting groups on the reactivity of ferrocene nucleus has been observed. It has been found that the effect of the electron-similar and of the electron-acceptor substituting groups was analogical to the effect of these compounds on the reactivity of benzene. This analogy with benzene was confirmed by a study of the basicity constants of ferrocenylamine, ferrocenylaminines and of dissociation constants of ferrocenylphenole. Study of the dissociation constants of ferrocenecarbonic and of substituted ferrocenecarbonic acids demonstrated presence of the previously unknown phenomenon - the transfer of conjugation through an atom of metal.

The effect of substitution on the reactivity of the ferrocene nucleus has been tracked.

The effect of electron-donor and electron-acceptor substitutes proved to be similar to their effect on the reactivity of benzene. This similarity to benzene was confirmed by the study of the basicity constants of ferrocenylamine and aniline ferrocenyl, and of the dissociation constant of phenol-ferrocenyl. The study of the dissociation constants of ferrocene-carbonic acids and substituted ferrocenium-carbonic acids, revealed the presence of the hitherto unknown phenomenon of conjunction transfer through the atom of a metal.

The meeting of October 16 was opened by academician M.I. Kabachnik who held a lecture titled "Double Reactivity and Dynamic Allatropy (tautomerism)". In this most interesting report, the lecturer pointed out that N.A. Nesmeyanov had clarified a significant section of theoretical organic chemistry dealing with the highly intricate problem of a double reactivity of organic compounds and tautomerism. In his works, A.N. Nesmeyanov has demonstrated that double reactivity and tautomerism are two completely different phenomena. Tautomerism means the equilibrium of isomers. It may well be the cause for double reactivity, but the latter may just as well occur on account of other, more generally, due to reasons involving the conjugation. On the basis of the study of the properties of quasi-complex compounds, N.A. Nesmeyanov put forward the representation of conjugation of prime and multiple bonds which, later, was extended to cover also the explanation for the double reactivity of the metallic derivatives of tautomeric systems. It was shown that the conjugation of prime bonds constitutes a very general feature in organic chemistry. As early as in 1950, N.A. Nesmeyanov re-examined on this basis, and from a new viewpoint, a wide range of material in the organic chemistry, and traced the display of conjugation in various reactions of organic substances. N.A. Nesmeyanov and M.I. Kabachnik have formulated the now widespread system of conjugation (π - π , π - σ , σ - σ , π - σ , σ - π , and p - p conjugations). The concept of prime-bond conjugation allowed A.N. Nesmeyanov to predict, and later on to find, a series of completely new directions of reactions, including such where a substance imitates the reactivity of its non-existent tautomer, forming a series of the latter's derivatives. After N.A. Nesmeyanov's suggestion, reactions of this type are designated as reactions occurring

"with reaction-center transfer". The general cause of double reactivity, not influenced by tautomerism, was found accordingly. The basic principles of tautomerism, discovered and pertaining to the basic acidity of tautomers, have been worked out. For the most significant case, which is prototropy, tautomeric equilibrium obeys the laws of protolytic basic-acidity equilibrium, whose general laws have been established by M.I. Kabachnikov. The phenomenon of tautomerism, itself, arises as a consequence of the double reactivity of the "common ion". New investigation methods, one of which is based on the stereospecific nature of the reactions of geometric isomers, have been worked out. In Mr Kabachnikov's laboratory, it was shown that in the case of "pseudomers", double reactivity arises solely as a result of the mechanism involving transfer of the reaction center. According to M.I. Kabachnikov, tautomerism and double reactivity, apart from being a theoretical problem of chemistry, also constitute a problem in the fields of chemistry which are of practical significance, such as organic pigments, polymers, and drug substances, as well as a problem of many of the most significant biological structures.

In his report, V.N. Kost gave a summary of the studies of the reaction of "telomerization" of polymers and ethylene that had been conducted in the "INEOS" of the Academy of Sciences. In the past years, A.N. Nesmeyanov and his collaborators have conducted a thorough study of the reactions of "telomerization", i.e., of controlled polymerization, which leads to substances with "mean" molecular weight, intermediate between polymers and monomers. Thoroughly investigated was the already known reaction of "telomerization" of ethylene with the carbon tetrachloride and chloroform, which has lead to a series of hitherto unknown α , α , α -trichloro- and α , α , α , α -tetrachloroalkanes used as the basic substances in the synthesis of various compounds. A simple method of obtaining ω -aminocarbonic acids was developed, which has become the basis for the industrial synthesis of ω -aminoenanthic acid and ω -aminopelargonic acid, whose polycondensation has yielded the new polyamide fibers "enant" and "pelargon", which are superior to caprone in many ways. There has been developed a simple way of synthesizing α -amino acids as well as higher dicarboxylic and hydroxycarboxylic acids, which are essential in the perfume industry.

Investigations of general interest for organic chemistry have been conducted in the course of this work. "Enant" fibers, and articles manufactured from them, were demonstrated in conclusion.

E. Ts. Chukovskaya reported on the "telomerization" reaction of olefin with silane, which was investigated under the guidance of A.N. Nesmeyanov. The thermal "telomerization" of olefin and silane with Si-H-bond content, as well as "telomerization" in the presence of a wide scope of catalysts were carried out successfully; this yielded a simple and convenient production method of dialkyldichlorosilane, which formerly was difficult to obtain, as well as of alkyltrichloro-silane. The synthesis of various heat-resisting polymers can be accomplished on the basis of these reactions.

O.V. Nogina, Cand. of Chem. Sci., reported on "The Synthesis and Properties of the Alkoxy-Derivatives of Titanium." In the field of the chemistry of transition elements, the alkoxy derivatives of titanium are being investigated under the guidance of A.N. Nesmeyanov. Methods of synthesizing different classes of the derivatives of tetravalent titanium have been developed in this field; their mutual transitions are under study. Derivatives of trivalent titanium have been obtained from tetraalkoxytitanates, from these, in turn, have been obtained the previously unknown manomeric dialkoxy-titanium-oxides, i.e., such compounds which have the $\text{W}=\text{O}$ bond (so rare in the chemistry of metalorganic compounds) between a transition element and oxygen. Their silicon- and titanium-ester addition products, are the "bricks" of which hetero-bonded polymers are built. A series of the compounds which were obtained, have valuable practical properties. A new significant physical phenomenon, that of disaggregation of associated alkoxy derivatives of titanium in time, has been observed in the study of the alkoxy derivatives of titanium.

N.K. Kochetkov, Dr. of Chem. Sci., spoke of the synthesis based on β -vinylchlorideketones. These substances are produced in a very simple way involving acetylene and acyl chlorides, and, on account of their high and variegated reactivity, have become the key-compounds in the field of the organic synthesis in the aliphatic, aromatic and, particularly, in the heterocyclic series. The synthesis of aliphatic compounds

is based on the exchange of a chlorine atom for that of another group, in a β -vinylchlorideketone. Its use in the alicyclic series is based on the fact that β -vinylchlorideketones are active diclefines. The condensation of β -vinylchlorideketones with compounds of the type of acetoacetic ester, leads to substituted salicylic acids. The method of the synthesis of alkyl-naphthalene has been developed on the basis of β -vinylchlorideketones. The most diverse application of β -vinylchlorideketones is in the synthesis of heterocyclic compounds. Five-membered heterocycles - the derivatives of pyrazole and isoxazole - have been produced; and of six-membered heterocycles, the derivatives of pyridine. This is by no means the limit of the possibilities revealed by β -vinylchlorideketones in the organic synthesis. Some of the compounds produced, constitute the parent substances in the synthesis of pharmacologically active preparations.

M. I. Rybinskaya, Cand. Of Chem. Sciences, spoke of the synthesis of heterocycles with an chirm hetero-atom based on β -vinylchlorideketones. Proceeding from β -vinylchlorideketones, there were produced salts of benzo- and naphtho-pyrilium and flavium, among them one natural salt, namely anthocyanidine. Of particular interest are the syntheses on the basis of β -vinylchlorideketones of heterocyclic compounds with ammonium nitrogen content of cycles. The lecturer told how she succeeded in closing cycles with the assistance of β -vinylchlorideketones and their derivatives, which led to the synthesis of substituted salts of dihydroquinolizine and the formerly unknown 1-aza- and 1,9-daza-analogues of dihydroquinolizine.

In his brief concluding speech, A.N. Nesmeyanov expressed his gratitude to all the lecturers for their information.

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